Powder Diffraction Standards

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The defining virtue of the powder diffraction technique is that it allows the user to probe all crystallographic reflections of a given d space range with a single scan. However, the para-focusing geometry of laboratory X-ray powder diffractometers offer data beset by a complex error function. Characterization of this error function, which is critical to the determination of accurate crystallographic and microstructural parameters, is one of the prime functions of NIST Standard Reference Materials (SRMs) for powder diffraction. Additional SRMs are used for quantitative analysis of multiphase mixtures.

While the d spacing and intensities of powder diffraction patterns can be calculated accurately from the crystal structure, the data within experimental patterns themselves embody aberrations specific to the powder diffractometer used for the measurement. The effect of these aberrations, convoluted with the profile of the radiation source, is generally referred to as the instrument profile function (IPF). Requisite to accurate characterization of the IPF is a standard which, due to its microstructure, imparts no discernable broadening to the diffraction profiles, and for which the lattice parameter is accurately determined. Production of a NIST Standard Reference Material, SRM, which meets these two criteria presents both a material and a metrological challenge.

The primary NIST line position SRM for powder diffraction, SRM 640b, silicon powder, was renewed this year as SRM 640c. Concurrently, the line profile SRM 660, lanthanum hexaboride, was renewed as SRM 660a. The line positions of both SRMs 640b and 660 were certified to a few parts in 10^5, which is entirely suitable for conventional data analysis techniques. However, to remain relevant for modern data analysis methods, it was necessary to improve the accuracy of the certified values by an order of magnitude. Furthermore, it was also desired to address the microstructure of both SRMs to render SRM 640c suitable for use as a line profile standard and to remove the slight amount of strain broadening known to affect SRM 660.

The uniformity of the ultra high purity, intrinsic silicon boules used as the feedstock for SRM 640c was verified prior to comminution. A total of 70 measurements covering the longitudinal and radial boule directions were performed on the NIST lattice comparison apparatus. The relative lattice variation of the input material implied from these measurements was $\pm$ 4 x 10^{-8} (95 % confidence level).

Comminution of the silicon boules was done via a jaw crusher followed by a jet mill. The powder was then annealed under gettered argon at 1000 °C for two hours. SRM 660a was prepared via a solid state process, jet milled, and annealed. Both SRMs offer a narrow particle size distribution; the mean of SRM 640c is $\cong$ 4.9 μm while that of while that of SRM 660a is $\cong$ 8.8 μm. However, the powder of SRM 640c consists of single crystal particles while that of SRM 660a consists of aggregates of crystallites.

The certification measurements were performed on a diffractometer built for first principles lattice parameter measurements. The metrologically intractable components of the IPF associated with a conventional diffractometer, *i.e.,* flat specimen, specimen position, beam penetration, and axis centration errors, were eliminated with the preparation of a parallel incident beam. The preparation optic also transmitted the $K_{\alpha1}/K_{\alpha2}$ emission spectrum of copper without distortion establishing the linkage to the International System of Units (SI). An auto-calibrating optical encoder that resulted in an angular measurement uncertainty of approximately 9.7 x 10^{-7} rad was used for *in situ* angle measurement. The 2θ zero error was eliminated by collecting profile data on either side of the incident beam. Diffracted beam analysis was performed with a high-resolution equatorial Soller collimator. Axial divergence of the incident and diffracted beam was limited by Soller slits.

The IPF of the parallel beam diffractometer was rigorously modeled using the Fundamental Parameters Approach to obtain the "true" profile positions. The refinement strategy constrained certain parameters, such as the one describing the transmission function of the equatorial Soller analyzer, across the entire pattern. Parameters specific to each profile, such as 2θ position, were refined independently. Results were considered as a plot of lattice parameters determined for each profile *vs.* 2θ. With ideal instrumentation and data analysis, the lattice parameters do not vary across 2θ. The most problematic aspect of the IPF was the axial divergence, which led to deviations at high and low angle. Certified values were those obtained from profiles of the 80 to 130 degrees 2θ region wherein the effects of axial divergence are minimal.

The lattice parameters of SRM 640c were certified to an accuracy of 4 parts in 10^6, those of SRM 660a were certified to an accuracy of 5 parts in 10^6. Furthermore, the preparation procedure of these SRMs resulted in microstructures which have virtually eliminated strain broadening in SRM 660a and will allow the use of SRM 640c as a line profile standard.

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